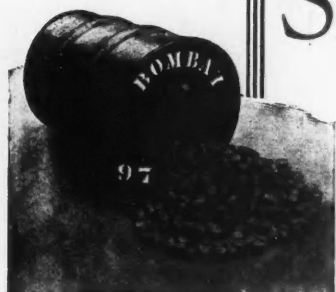


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VOLUME XIV. NUMBER 6

JUNE 1941

Properties of Pozzolana.

Determining Suitable Proportions of Pozzolana to Cement and Lime.

AN investigation into the effect on Portland cement and lime of adding various quantities of pozzolana has been made by Messrs. H. M. Larmour, E. L. McMaster and W. Jaques, of the Yosemite Portland Cement Corporation of California. The results of the investigation, of which an abstract is given in the following, are given in *Rock Products* for March, 1941.

The authors state that a review of test methods led them to decide that the procedure outlined by Prof. R. E. Davis for the proposed Bonneville Dam held the most promise. Essentially this specification was a strength test of pozzolana-lime-sand mortar specimens, stored successively at 70 deg. F. for 12 hours; then at 100 deg. F. for 12 hours; then at 130 deg. F. until 12 hours before testing, and then at 70 deg. F. for the final 12-hours period before testing. The specimens were tested at 7 and 28 days.

The idea of using higher temperatures to accelerate pozzolanic activity seemed logical; it was believed that this activity would increase progressively with higher temperatures and pressure in a saturated atmosphere. It was further believed that this progressive pozzolanic activity could be measured by the decrease in the insoluble residue. If a pozzolana reacts with lime when the two are mixed together as a paste and cured, the extent of such reaction should be manifested by a decrease in the insoluble residue of the mixture as hydration progresses.

The siliceous materials in Table 1 were selected and properly prepared for pozzolanic tests. As a pilot, Friant pumicite, a pozzolana of well-established reputation, was used. Using the oxide analysis as a basis, hydrated lime was mixed with each of these siliceous materials in sufficient proportions to form

TABLE 1.—SILICEOUS MATERIALS USED FOR TEST.

	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	Insoluble
Fresno Pumicite	74.72	2.79	12.10	1.01	.53	95.85
Ottawa Sand	96.25	1.24	.62	1.21	.29	99.45
Oakdale Sand	66.85	5.92	14.63	5.65	1.89	90.18
*Alusite	51.80	5.60	40.15	1.45	.10	96.75
Montmorillonite	56.97	7.59	21.24	7.13	2.39	87.68
The lime used:					Loss	
Hy-Tex (hydrated)	3.24	.25	2.10	69.79	.98 22.86	1.12

mono-calcium-silicate. Each mixture was gauged with water (40 per cent.), stored for 24 hours at 70 deg. F., and then autoclaved at 300 lb. for six hours. The initial insoluble residues (prior to autoclaving) and the final insoluble residues (after autoclaving) are shown in Table 2.

TABLE 2

	Initial Per cent.	Final Per cent.
Fresno pumicite	52.10	1.53
Ottawa sand	49.56	5.37
Oakdale sand	47.13	9.00
Montmorillonite	54.56	13.20

In the second test the hydrated lime was increased by 10 per cent. to note its effect, with the results shown in Table 3. The second addition of lime indicated that in the first trial an excessive amount of pozzolana had been used for the lime addition.

TABLE 3

	Initial Per cent.	Final Per cent.
Fresno pumicite	51.20	1.09
Ottawa sand	43.90	3.02
Oakdale sand	43.70	7.44
Montmorillonite	51.50	6.95

TABLE 4.—DETERMINING INSOLUBLE RESIDUES OF LIME-POZZOLANA MIXTURES.

Hydrated Lime	Puzzolan Friant Pumicite	Initial Insoluble %	Temper- atures	Insoluble Residue %					5 Months
				3 Days	12 Days	28 Days	60 Days	90 Days	
51.0%	49.0%	52.10	70° F	50.7	50.3	47.02	45.12	41.34	31.58
51.0%	49.0%	52.10	110° F	46.7	40.0	38.60		36.50	
51.0%	49.0%	52.10	150° F	43.4	38.1	36.78	35.08	32.25	
51.0%	49.0%	52.10	212° F	38.0	34.3	28.51	24.09	14.66	
Ottawa Sand									
56.5%	43.5%	49.56	70° F	48.2	47.9	47.46	48.66	48.55	43.46
56.5%	43.5%	49.56	110° F	48.4	47.3	46.27	46.12	44.97	
56.5%	43.5%	49.56	150° F	40.7	40.7	33.80	25.72		
56.5%	43.5%	49.56	212° F	35.7	33.7	13.15	12.22	10.31	
Oakdale Sand									
54.5%	45.5%	47.13	70° F	46.0	46.0	45.79	44.97		41.44
54.5%	45.5%	47.13	110° F	47.0	39.9	40.60		40.80	
54.5%	45.5%	47.13	150° F	42.8	40.5	32.83	28.77	24.04	
54.5%	45.5%	47.13	212° F	33.9	18.77	16.1	15.25	12.25	
Montmorillonite									
43.3%	56.7%	54.56	70° F	52.7	48.9	48.9	48.9	46.57	33.67
43.3%	56.7%	54.56	110° F	49.4	47.4	41.56	39.2	37.97	
43.3%	56.7%	54.56	150° F	30.8	33.3	29.35	26.6		
43.3%	56.7%	54.56	212° F	29.6	23.5	17.36	14.87	14.87	

TABLE 5.

	Initial Insoluble %	Final Insoluble %	Soluble %
51.0% Hyd. lime plus 49.0% Pumicite	52.10	1.53	50.57
56.5% Hyd. lime plus 43.5% Ottawa Sand	49.56	5.37	44.19
54.5% Hyd. lime plus 45.5% Oakdale Sand	47.13	9.00	38.13
43.3% Hyd. lime plus 56.7% Montmorillonite	54.56	13.20	41.36

TABLE 6.

	70 deg. F			110 deg. F			150 deg. F			212 deg. F		
	28	90	Days	28	90	Days	28	90	Days	28	90	Days
Hyd. Lime & Pumicite...	10.04%	21.28%	26.70%	30.85%	30.29	38.25	46.64	74.04				
Hyd. Lime & Ottawa Sand	2.29%	4.75%	7.45%	10.39%	35.66	53.95	82.39	88.82				
Hyd. Lime & Oakdale Sand	3.51%	5.66%	17.13%	16.60%	37.50	60.56	81.38	91.48				
Hyd. Lime & Montmorillonite	13.68%	19.32%	31.43%	40.11%	60.95	67.60	89.94	95.96				

TABLE 7.—TESTS WITH PORTLAND CEMENT AND POZZOLANAS.

	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₂	Loss	Free Lime	In-sol.	C ₂ AF	C ₂ A	C ₂ S	CaSO ₄	MgO
High-Early (Portland)	22.40	1.92	3.84	66.09	1.51	2.51	1.32	1.00	.16	5.84	6.92	59.91	18.66	4.27 1.51
Low-Heat (Portland)	24.22	4.23	5.23	61.29	1.70	1.69	.73	.50	.56	12.86	6.68	21.53	51.62	2.87 1.70
Pumicite (Dry Basis)	74.72	2.79	12.10	1.01	.53	—	—	—	95.85					
Alusite (Dry Basis)	51.80	5.60	40.15	1.45	.10	—	—	—	96.75					

In order to show how this autoclave test might be reconciled for evaluating the worth of a pozzolana under field conditions, parallel tests, storing the specimens at temperatures of 70 deg. F., 110 deg. F., 150 deg. F., and 212 deg. F., were made and insoluble residues determined after curing periods of 3, 12, 28, 60, 90 and, in some cases, 150 days. These results are given in Table 4. It might be well to consider the progress of the reaction by showing the percentage decrease of the insoluble residue at 28 and 90 days for all temperatures. This will be a measure of the reaction. As a basis for presenting the results, it is assured that the difference between the initial insoluble residue (before autoclaving) and the final insoluble residue (after autoclaving) represents the total amount of reaction. This is shown in Table 5 as percentage soluble.

The degree of reaction at any particular time and temperature is then calculated by determining the difference between the initial and the observed insoluble residue at the time and temperature desired. This difference is expressed as a percentage of the total soluble shown in Table 5.

Table 6 shows the progress of the reaction, as expressed in percentage of total soluble for four temperatures at periods of 28 and 90 days. These results, using hydrated lime with siliceous materials, indicated that the reaction proceeded regardless of temperature, but rates of reaction were greatly increased with temperature.

The authors next carried out similar tests with Portland cements and pozzolanas. It was decided to use a high- and low-limed cement for the first trials. Two siliceous materials were selected as pozzolanas, namely Friant pumicite and alusite. The analyses for these four materials are given in Table 7. The fineness detail of the materials is given in Table 8.

TABLE 8

	Minus 325 mesh Per cent.
Alusite	96
Pumicite	98
High-lime cement	97
Low-lime cement	94

Mixtures of the cements and pumicite were made up in increasing percentages of the pumicite as shown in Table 9. The mixtures were gauged with water (40 per cent.), allowed to cure for 24 hours at 70 deg. F., and then autoclaved for 24 hours at 100 lb. and then for six hours at 300 lb. pressure. The final insoluble residue for each mix is shown in Table 9.

The results indicate that for the given conditions of temperature, pressure and humidity, this particular pozzolana (Friant pumicite) has been quantitatively measured beyond lime saturation. To investigate a pozzolana of unknown activity, alusite was selected for parallel comparison with the Friant pumicite. The results of this test are given in Table 10.

Considering Friant pumicite and alusite, it will be noted that Friant pumicite gave much better results in all cases but one (which may be an error) than alusite.

TABLE 9.—TESTS WITH FRIANT PUMICITE.

Cement Used	% (Wt.) Cement	% (Wt.) Pumicite	Autoclaved % Insoluble
High early	83.3	16.7	1.39
High early	76.9	23.1	1.59
High early	71.4	28.6	3.32
High early	65.0	35.0	3.03
High early	45.0	55.0	20.93
Low-Heat	83.3	16.7	0.91
Low-Heat	76.9	23.1	1.12
Low-Heat	71.4	28.6	1.80
Low-Heat	65.0	35.0	4.48
Low-Heat	45.0	55.0	39.33

TABLE 10.—TESTS WITH ALUSITE.

Cement Used	% (Wt.) Cement	% (Wt.) Alusite	Autoclaved % Insoluble
High Early	83.3	16.7	6.31
High Early	76.9	23.1	8.49
High Early	71.4	28.6	10.81
High Early	65.0	35.0	13.27
High Early	45.0	55.0	33.32
Low-Heat	83.3	16.7	6.61
Low-Heat	76.9	23.1	9.29
Low-Heat	71.4	28.6	12.01
Low-Heat	65.0	35.0	13.99
Low-Heat	45.0	55.0	37.80

TABLE 11.—DETERMINING SiO_2 AND R_2O_3 FROM INSOLUBLE SAMPLES.

				Insoluble Analysis	
				SiO_2	R_2O_3
High Early Cement 83.3%	Pumicite 16.7%	Insoluble 1.39		79.48	5.69
High Early Cement 71.4%	Pumicite 28.6%	Insoluble 3.32		91.27	2.93
Low-Heat Cement 83.3%	Pumicite 16.7%	Insoluble .91		74.69	9.58
Low-Heat Cement 71.4%	Pumicite 28.6%	Insoluble 1.80		80.30	13.31
Average				81.43	7.88
High Early Cement 83.3%	Alusite 16.7%	Insoluble 6.31		63.95	35.50
High Early Cement 71.4%	Alusite 28.6%	Insoluble 10.81		66.30	31.85
Low-Heat Cement 83.3%	Alusite 16.7%	Insoluble 6.61		72.40	27.55
Low-Heat Cement 76.9%	Alusite 23.1%	Insoluble 9.29		69.05	28.15
Average				67.92	30.78

The insoluble residue from several of the autoclaved specimens was analysed and compared with the non-autoclaved pozzolana. Using the insoluble samples obtained from the tests shown in Tables 9 and 10, SiO_2 and R_2O_3 were determined as shown in Table 11.

Comparing these averages with the original analysis of the pozzolanas it is seen that :

	SiO_2 Per cent.	R_2O_3 Per cent.
Pumicite insoluble (average)	81.43	7.88
Pumicite (Table 1)	74.72	14.89
Alusite insoluble (average)	67.92	30.76
Alusite (Table 1)	51.80	45.75

These results show that proportionally more of the R_2O_3 has been rendered soluble than the silica as measured by this method. The increase in the ratios of SiO_2 to R_2O_3 for the Friant pumicite and alusite was approximately the same, in spite of the fact that the alusite contained a much greater percentage of R_2O_3 . For the pumicite the R_2O_3 group decreased by 47.07 per cent. and the alusite by 32.76 per cent. The SiO_2 for both the pumicite and alusite showed an increase in the autoclaved sample. This increase amounted to 8.98 per cent. for the pumicite and 31.11 per cent. for the alusite.

The results from the work done with the autoclave would hardly be applicable for anticipating activity under field conditions where curing progresses at much lower pressures and temperatures. To measure the activity of pozzolanas with Portland cement at various temperatures, a similar test was arranged as carried out with the lime-pozzolana mixtures (see Table 4). As in the lime-pozzolana tests, the specimens were mixed with a definite percentage of pozzolana and cement, gauged with 40 per cent. of water and stored in sealed metal containers at 70 deg. F., 110 deg. F., 150 deg. F., and 212 deg. F. for varying lengths of time. At each period an insoluble determination was made on each specimen. These results are shown in Table 12.

The "initial insolubles" were determined in each case by analysis of each prepared mixture. The "autoclaved insolubles" are the results after two five-hour periods of autoclaving at 300 lb. pressure. An intervening pulverising (mortar and pestle) was made before the second autoclaving. The "soluble" increases with higher percentage additions of pozzolana. This is not unreasonable when it is considered that both the hydration of the cement and absorption of the lime in solution by the particles of pozzolana are both surface reactions, and it is reasonable to expect that, with a higher percentage of pozzolana available for surface reaction with lime in solution, slightly more will react. The results of Table 12 are shown in Table 13 in terms of percentage completion of activity, together with compressive strengths. The percentage "reactive" was determined, calculated and expressed as shown in Table 6. The mortars were 1 : 2.75 mix, using a local concrete sand. The water was added to give a definite flow

TABLE 12.—DETERMINING INSOLUBLE RESIDUES OF PORTLAND CEMENT-POZZOLANA MIXTURES.

Cement	Puzzolan	Initial Insoluble	Autoclave Insoluble	Soluble	Days	% Insoluble Residue for Time and Temperature			
						70° F.	110° F.	150° F.	212° F.
70% Modified	30% Friant Pumicite	27.64	0.78	26.86	28	25.80	19.08	16.29	11.03
				26.86	90	23.44	18.21	14.35	7.99
				26.86	180	20.82	17.61	10.91	6.99
55% Modified	45% Friant Pumicite	41.20	11.49	26.86	365	17.38	16.03	8.92	4.93
				29.71	28	39.88	32.99	31.47	28.75
				29.71	90	36.86	31.02	28.47	20.16
70% Modified	30% Ground Ottawa Sand....	29.97	8.37	26.86	180	34.63	30.66	29.06	17.33
				29.71	365	30.89	29.38	20.07	16.59
				21.60	28	29.84	29.02	26.11	14.03
55% Modified	45% Ground Ottawa Sand....	43.00	18.74	21.60	90	29.71	28.63	22.34	11.87
				21.60	180	29.50	.	.	11.60
				21.60	365	25.97	.	.	11.02
55% Modified	45% Ground Ottawa Sand....	43.00	18.74	24.86	28	43.38	43.04	37.87	26.27
				24.86	90	43.33	41.96	29.14	23.73
				24.86	180	43.03	40.80	24.54	21.62
55% Modified	45% Ground Ottawa Sand....	43.00	18.74	24.86	365	39.99	38.34	22.57	21.10
				24.86	365	39.99	38.34	22.57	21.10
				24.86	365	39.99	38.34	22.57	21.10

TABLE 13.—RESULTS OF INSOLUBLE RESIDUE DETERMINATIONS IN TERMS OF PERCENTAGES OF POZZOLANIC ACTIVITY AND COMPRESSIVE STRENGTH.

Cement	Puzzolan	Mortars	Sand	W/C	Days	70 deg. F. P.S.I. Reactive	110 deg. F. P.S.I. Reactive	150 deg. F. P.S.I. Reactive	212 deg. F. P.S.I. Reactive
Mod. 100%	None		1:2.75	.562	28	5156	6302	4488	3724
Mod.	None		1:2.75	.562	90	7735	8435	4870	4488
Mod.	None		1:2.75	.562	180	8117	7990	5093	4998
Mod.	None		1:2.75	.562	365	8339	8530	7276	6812
Mod.	Pumicite	30%	1:2.75	.571	28	4376	4169	4169	5092
Mod.	Pumicite	30%	1:2.75	.571	90	5982	5825	4647	5347
Mod.	Pumicite	30%	1:2.75	.571	180	7066	6884	5762	7958
Mod.	Pumicite	30%	1:2.75	.571	365	7763	6363	7958	7763
Mod.	Pumicite	45%	1:2.75	.596	28	2769	4138	3183	4249
Mod.	Pumicite	45%	1:2.75	.596	90	5555	4679	4297	5602
Mod.	Pumicite	45%	1:2.75	.596	180	5093	5347	4647	8276
Mod.	Pumicite	45%	1:2.75	.596	365	6494	6303	7003	7576
Mod.	Grd Ottawa	30%	1:2.75	.571	28	3883	4138	4934	6844
Mod.	Grd. Ottawa	30%	1:2.75	.571	90	5252	5093	5666	8276
Mod.	Grd. Ottawa	30%	1:2.75	.571	180	5157	5347	7194	9704
Mod.	Grd. Ottawa	30%	1:2.75	.571	365	5602	5539	8212	8753
Mod.	Grd. Ottawa	45%	1:2.75	.597	28	2515	2865	4807	5762
Mod.	Grd. Ottawa	45%	1:2.75	.597	90	3310	3550	5816	7630
Mod.	Grd. Ottawa	45%	1:2.75	.597	180	3549	4170	6111	7687
Mod.	Grd. Ottawa	45%	1:2.75	.597	365	3852	4265	6716	9135

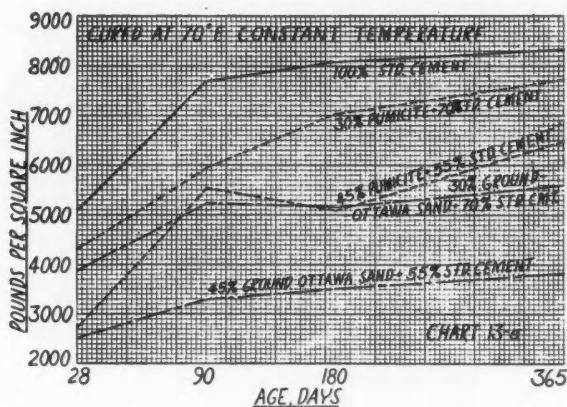


Chart 13(a).—Strengths of Mortars cured at 70 deg. F.

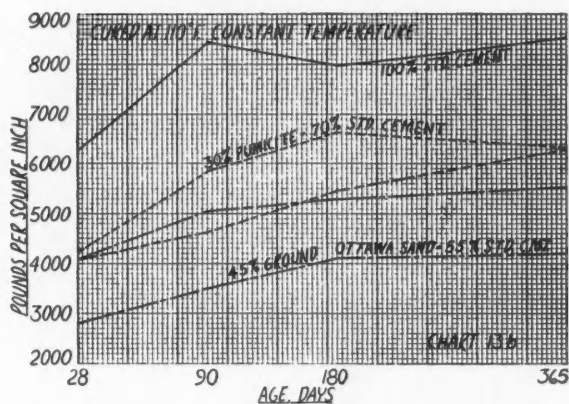


Chart 13(b).—Strengths of Mortars cured at 110 deg. F.

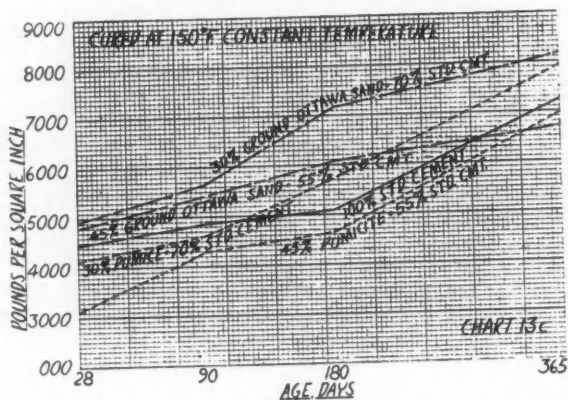


Chart 13(c).—Compressive Strengths of Mortars cured at 150 deg. F.

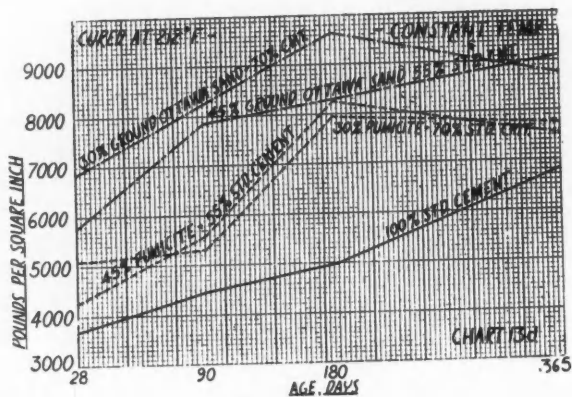


Chart 13(d).—Compressive Strengths of Mortars cured at 212 deg. F.

for all mixes. The strength specimens were cast in 2-in. by 4-in. sealed metal containers. As a precautionary measure the 2-in. by 4-in. specimens were placed in one-gallon friction-top cans partly filled with water and sealed to ensure a moist curing atmosphere. The specimens were stored at the designated temperatures and tested at the periods shown.

The compressive results for 28, 90, 180, and 365 days, at constant temperature for each mixture shown in Table 13, are illustrated by Charts 13-a, b, c, d, showing strength gain with time at 70 deg. F., 110 deg. F., 150 deg. F., and 212 deg. F., respectively.

It is to be noted that at 70 deg. F. and 110 deg. F. the 100 per cent. Portland cement mortar strength leads the Portland-pozzolana cement mortars at all periods. This seeming strength advantage is in the reverse order at temperatures above 110 deg. F. At temperatures between 110 deg. F. and 150 deg. F. (as shown by results at 150 deg. F.), the 100 per cent. Portland cement mortar has lost the strength advantage it held at 70 deg. F. and 100 deg. F. It is also to be noted that the strength gain from 110 deg. F. to 150 deg. F. for the Portland-pozzolana mortar made with ground Ottawa sand is much greater than the Portland-pozzolana mortar cement made with pumicite. At 212 deg. F. the 100 per cent. Portland cement mortar strength has been exceeded by all of the Portland-pozzolana mortars. Of the two Portland-pozzolana mortars, the ground Ottawa sand has higher strengths. By contrast, the strength results of the pumicite Portland-pozzolana mortar at 70 deg. F. and 110 deg. F. exceed the ground Ottawa Portland-pozzolana mortar.

Parallel specimens of all of the above mortar mixes were autoclaved for strength after curing for 24 hours at 70 deg. F. The results are tabulated in Table 14. The sealed specimens were autoclaved continuously at two pressures. The first pressure was 100 lb. for 24 hours and was then raised to 300 lb. and held for 24 hours.

TABLE 14.—AUTOCLAVE STRENGTH TESTS

Cement Per cent.	Pozzolana Per cent.	Autoclave strength lb. per sq. in.
100	None	4536
70	30 Pumicite	6494
55	45 Pumicite	5650
70	30 Ground Ottawa sand	7623
55	45 Ground Ottawa sand	8308
70	30 Ground alusite	4616
55	45 Ground alusite	3756

Here again it is to be noted that at high temperature curing the 100 per cent. Portland cement mortar strength is low. Portland-pozzolana mortar made with

ground Ottawa sand exceeds in strength the Portland-pozzolana mortar made with pumicite. These results conform with previous results obtained at 212 deg. F. for longer periods of time and detailed in Table 13. The Portland-pozzolana mortar made with ground alusite shows low strengths at high temperatures.

The foregoing information shows a method for selecting a type of pozzolana for a particular purpose. For thin slabs, rendering, or structures where heat loss

TABLE 15.—EFFECT OF FINENESS OF POZZOLANA.

Curing Time Days	% Std. Cement	% Pumicite	Pumicite Fineness	% Reactive at 70 deg. F.	% Reactive at 110 deg. F.	% Reactive at 150 deg. F.	% Reactive at 212 deg. F.
7	60% Std.						
	1900 sq. cm. per gr.	40%	76%-325M	1.83	21.70	25.59	28.2
28	1900 sq. cm. per gr.	40%	76%-325M	8.25	25.70	29.0	36.3
60	1900 sq. cm. per gr.	40%	76%-325M
120	1900 sq. cm. per gr.	40%	76%-325M	31.90	41.23	44.6	53.2
7	60% Std.						
	1900 sq. cm. per gr.	40%	98%-325M	8.03	37.70	43.6	44.8
28	1900 sq. cm. per gr.	40%	98%-325M	31.08	59.2
60	1900 sq. cm. per gr.	40%	98%-325M	...	56.04	55.9	...
120	1900 sq. cm. per gr.	40%	98%-325M	50.70	56.70	60.5	72.3

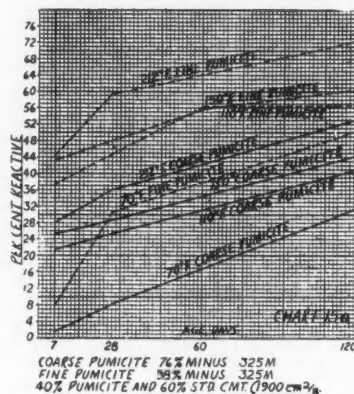


Chart 15(a).—Graphical Interpretation of Table 15.

by radiation is high, a pozzolana having a high reactive rate at normal temperatures will correct or lessen unsightly "bloom." For mass concrete, such as dams, where high curing temperatures prevail, pozzolanas having a low reactive rate at normal temperatures but increasing with temperature may be preferred for ultimate strength.

Consideration of the fineness detail for a pozzolana should not be overlooked. To show this, a coarse and fine pozzolana (pumicite) of the same chemical composition were compared for "reactivity," using the same cement. The fineness of the coarse and fine pumicite was 76 per cent. and 98 per cent. minus

the 325-mesh sieve. Table 15 shows the comparison and Chart 15A shows the results graphically.

Commenting on Table 15 and chart 15A, fine pumicite "reactivity" exceeds the coarse pumicite for all comparative temperatures. After 28 days the 70 deg. F. fine pumicite exceeds the coarse pumicite even at 150 deg. F. At 110 deg. F. the seven-day fine pumicite has a "reactive" rate equal to 99 days for the coarse pumicite at 110 deg. F., 81 days at 150 deg. F., and 37 days at 212 deg. F.

SUMMARY.

The lower strengths at the early periods for Portland-pozzolana cement mortars and concretes when normal curing temperatures prevail can be decidedly improved by increasing the fineness of the cement. It is possible in many cases to accomplish this increased surface area of the cement at a saving when the pozzolana displacement offsets the increased grinding cost.

The ultimate reactivity of a pozzolana may readily be obtained with the autoclave. Trial additions of a pozzolana with hydrated lime are autoclaved and the decrease in the insoluble residue determined. The rate of activity with strength gain for any Portland-pozzolana mix may readily be determined and compared on parallel specimens cured at two or more constant temperature ranges for like periods of time. Pozzolan action of silicates is influenced by chemical composition and curing temperature. Silicates having low or no alumina are slowly reactive at normal curing temperatures, but are highly reactive at high curing temperatures. Siliceous materials containing comparatively high R_2O_3 contents do not show as concordant results between solubility and mortar strength tests as those siliceous materials with lower R_2O_3 content. A desirable fineness of the selected pozzolana may be determined for any curing temperature by the outlined test for activity. Grinding the pozzolana removes surface films from the particles and greatly accelerates activity.

Dispersion Agents in Portland Cement.

THE effect of dispersion or deflocculation of Portland cement was described by Dr. E. W. Scripture in a paper published by the Master Builders' Company of Cleveland, Ohio, of whose laboratory Dr. Scripture is the director. In the course of this paper the author points out that the operation of dispersing agents has been used for a long time, for example, in the ceramic industries for the deflocculation of clay slips. Until recently no dispersing agents were known which were applicable to the deflocculation of Portland cement. The dispersion or deflocculation of Portland cement in a concrete or mortar mix is important in a number of aspects. In general, the reactions on which Portland cement depends for its properties are surface reactions. They are, therefore, a function of the surface area of the cement, and for this reason cement manufacturers have increased the fineness of grinding. Unfortunately the full surface area produced by fine grinding is not available for reaction, due to the flocculated condition of the cement in the mix; this agglomerating tendency is even greater with greater fineness, so that the beneficial effects of fine grinding have been in some measure offset by the formation of lumps. The addition of a dispersing agent to Portland cement mixes makes available for reaction the full surface area of the cement particles, and permits the use of the cement to the full extent.

To produce colour in a concrete structure, pigments are incorporated with the cement, and in some cases coloured aggregates are used. In such an application a cement dispersing agent offers advantages in relation to the properties of the concrete or mortar, and also effects improvements with respect to the pigment. The dispersing agent facilitates the dissemination of the pigment uniformly throughout the mix, increases the brilliance of the resulting colour, produces equal colour with less pigment, and overcomes the deleterious effects of some pigments.

Effect on Properties of Concrete.

Since the properties of concrete and mortar are primarily dependent on the amount and quality of the cement paste, any influence which alters the nature of this paste will influence the properties of the mix. Dispersion of the cement basically changes the relations of the solid particles to the liquid, and consequently may be expected to have a profound influence on many of the characteristics of the concrete or mortar. These effects may be divided into two groups corresponding to the two states in which concrete exists: (1) the transitory plastic stage during placing, and (2) the ultimate hardened mass.

The plastic state is the period during which the concrete or mortar is placed, compacted, and finished. Unless the mix is workable at this time, a sound structure will not be produced regardless of any other properties of the mix. This property of workability may be considered as made up of (a) mobility or ease of flow, and (b) cohesiveness or resistance to segregation. Dispersion of the cement particles will increase mobility or ease of flow. This is because the water held in the lumps or agglomerates of the flocculated cement is released to

become a part of the fluid medium through which the particles move. Further, by breaking up these lumps, the size of the units in the liquid is reduced so that they can move more easily past each other in the fluid. The result is a more workable concrete produced with less water.

Cohesiveness is attributable to the attractive forces between surfaces. Therefore, dispersion of the cement which makes available a greater surface area will increase the cohesiveness of the mix. A first result is that the mix becomes "fatter." A more generally important effect is a reduction of the tendency of the components of the mix to separate. The aggregate is less apt to separate from the cement paste, so that the danger of honeycombing is minimised. In its upward movement through the mix the water tends to collect under the larger pieces of aggregate, forming pockets on the underside so that the aggregate is not bonded to the cement paste. Separation of the water and fines in an upward direction from the coarser part of the mix is prevented. By this means "bleeding" or "watergain" and the formation of laitance are eliminated or reduced, and the uniformity of the mix in place is enhanced.

A further effect of dispersion, also due to the greater surface area available, is a greater force holding the water to the cement particles. This produces higher "water retentivity," which is particularly important in masonry mortars where porous masonry units tend to suck water out of the mortar. The volume changes which occur during the hardening of concrete are in all probability more important than those which take place subsequently. They are caused by movement of water from one part of the mix to another, and by loss of water from the mix by suction, by evaporation, or by other means. Dispersion of the cement counteracts these volume changes, first by reducing the amount of water required for a workable mix, and second by imparting higher water retentivity, thus resisting movement and loss of water.

The effects of dispersion of the cement particles on plastic concrete or mortar may be summarised as follows: (1) More workable concrete with less water; (2) increased "fatness"; (3) reduced segregation and bleeding; (4) greater water retentivity; (5) reduced shrinkage before hardening.

Dispersion affects practically all the important properties of the hardened concrete or mortar. This is due primarily to two causes. First, the reduction of the amount of water required in the mix; secondly, the dispersion of the cement particles produces a finer grained structure in the cement paste and an increased surface area such that the hydration reactions of the cement proceed more effectively. Some of the more important properties may be considered in somewhat more detail.

Durability.—Since the attack of corrosive solutions is a reaction occurring at the surface where the solution comes in contact with the cement, the rapidity of attack is dependent on the ability of the corrosive solution to penetrate into the structure and on the ability of the cement to resist attack. The ability of the solution to penetrate is governed by the same factors which contribute to watertightness. Hence, a dispersing agent increases resistance to corrosion.

Disintegration by freezing and thawing is primarily dependent on the ability of water to penetrate into the concrete and on the strength of the cement paste to resist this force. Since a dispersing agent reduces permeability and in other ways makes the concrete more watertight, and since it also increases strength, it will increase resistance to freezing and thawing.

Watertightness.—Watertightness is dependent on freedom from defects, freedom from cracks, and on permeability. Since the use of a dispersing agent results in an improvement in all these respects it will increase watertightness.

Strength.—Strength will be increased by the reduction of water made possible by dispersion. The greater surface area made available by dispersion also leads to greater and more rapid hydration, so that further improvements in strength are obtained.

Permeability and Absorption.—Permeability and absorption are proportional to the volume of excess water per unit volume of concrete. The reduction in the excess water required for workability by the use of a dispersing agent reduces permeability and absorption.

Volume Change.—Volume change is proportional to the volume of cement paste per unit volume of concrete. Reduction in the water reduces volume change.

Uniformity.—The uniformity of the hardened structure and freedom from defects will be improved due to the improvement in the properties of the plastic mix.

The effects of a dispersing agent on the properties of the hardened concrete or mortar may be summarised as follows: (1) Increased durability and longer life; (2) increased watertightness; (3) higher strength; (4) lower volume change; (5) lower permeability or absorption; (6) greater uniformity and freedom from defects.

Conclusion.

Improvements to be expected in the properties of concrete will follow from methods which permit excess water to be reduced. A cement dispersing agent radically alters the physical nature of the paste in such a manner that workability can be attained with a substantial reduction in the water required. This in turn improves durability, watertightness, strength, volume change, and other properties. Since the many applications of cement mixes require some variations in the properties of the different mixes, some modifications of, or additions to, the cement dispersing agent may be desirable; but the principle of reduction in water content by means of dispersion will remain beneficial.

Determination of Particle Size.

A SYMPOSIUM on methods of determining the size of particles smaller than can be measured by sieves was held in connection with a meeting of the American Society for Testing Materials at Washington in March last. A number of papers were presented, and these are abstracted as follows in the March, 1941, number of *Concrete* (Cement Mill Section).

By P. H. EMMETT.—Within the past five years a new method has been worked out for measuring the surface area of finely-divided or porous solids by the use of low-temperature adsorption isotherms. This method applied to non-porous materials affords an additional means of obtaining values for the average particle size of a substance. The surface-area measurements depend upon making adsorption isotherms of some gas, such as nitrogen, near its boiling point and then selecting on the isotherm the volume of gas corresponding to a monolayer. A simple multiplication of the number of molecules in such a monolayer by the average cross-sectional area of the molecules yields a value for the surface area. Details of the apparatus and procedure, including the application of a theoretically-derived equation for estimating the volume of adsorbed gas in the monolayer, have been described in the literature. Application of the method to several hundred miscellaneous materials, and comparison of results wherever possible with those obtained by other means, has continued to strengthen confidence in its reliability and reproducibility.

The calculation of the average particle size of a finely-divided non-porous material from the surface area obtained by this gas adsorption method entails the same types of uncertainty due to shape factors and methods of averaging that are involved in any method for estimating particle diameters from measurements of the total surface area of the particles. In addition, the proposed method has the following limitations as applied to measuring particle size: (1) it cannot be applied to porous materials; (2) the surface area of a 25 c.c. sample of a powdered substance must be as large as about 10,000 sq. cm. if the results are to be reproducible to 5 per cent. On the other hand, the method has the advantage of being applicable to particle sizes too small to measure by any other method. Excellent agreement with the direct microscopic method has been obtained on sized glass beads 5 microns in diameter and with the ultra-microscopic particle count method as applied to zinc oxide pigments in the 0.1 to 0.3-micron range.

By W. W. EWING.—The specific surface of pigments can be determined by adsorbing wetting agents on the surface from solutions. This entails (1) the selection of a solute which is preferentially adsorbed on the pigment; (2) the selection of the correct solvent; (3) the preparation of the pigment surface; and (4) a knowledge of the cross-sectional area of the adsorbed molecule in its oriented position. Successful experiments have been carried out on various zinc oxide pigments using anhydrous benzene as the solvent and methyl stearate and ethylenedipalmitate as the adsorbents.

By S. W. MARTIN.—The information available on the determination of subsieve particle size distributions is examined for solid-liquid systems in terms of two fundamental principles, namely, (1) the cumulative settling law for a polydis-

perse material, (2) Stokes's frictional resistance law for a moving spherical particle. On the basis of the cumulative settling law, gravitational and centrifugal sedimentation procedures are classified into cumulative, accurate incremental, and approximate incremental methods. The theory underlying each category is considered and literature citations are made for purposes of illustration and confirmation of particle-size distribution values which are obtainable from sedimentation methods. Finally, the inherent advantages as well as restrictions which must be imposed for valid results are critically evaluated.

BY P. C. CARMAN.—The paper gives a full description of the experimental technique and discusses the limitations of the permeability method, and presents new data relating to the shape of non-spherical particles. While the experimental evidence is inconclusive, it would appear that the method tends to give somewhat high values of the specific surface for very fine particles, particularly for very heterodisperse powders extending down to colloidal dimensions.

BY L. T. WORK AND H. E. SCHWEYER.—A review is given of methods proposed for determining the size distribution of polydisperse materials of such size that the majority of the particles are above the colloidal range. As a guide to the selection of a method for a particular purpose, a summary is given and means of representing the data are discussed. A table of nomenclature is included.

BY P. S. ROLLER AND P. V. ROUNDY.—The size distribution of several Portland cements was determined by an absolute method involving the use of a particle size of air analyser, and, from the data, surface area was calculated by a statistical procedure. Determinations on the same cements were also made by the Wagner turbidimeter and by an air permeability method after Gooden and Smith. In the latter method the conversion factor to a smooth cube particle was ascertained by testing several cement fractions. Surface areas obtained by the various methods were compared and discussed. Size constants other than surface area, such as coefficients of uniformity and regression, which are obtained only from distribution data, have been considered, and simplified methods of calculations indicated.

BY J. HILLIER.—The useful magnification of microscopes using visible or ultraviolet light is limited to about 3,000 diameters, due to the relatively long wavelength of the observing medium. High-velocity electrons, which have an extremely short effective wavelength, can, with the aid of electron optics, be used in an electron microscope to obtain magnifications that are about 100 times greater than those obtained with a light microscope. The electron microscope embodies principles similar to those employed in an optical microscope, with magnetic electron lenses taking the place of glass lenses. An electron microscope capable of very high resolution and suitable for general laboratory use has been built in the R.C.A. laboratories. This instrument is rugged, simple to operate, and completely self-contained. Specially designed power supplies provide the extremely constant voltage and current supplies required for its operation. This new microscope, which is capable of resolving detail finer than 50 Å, finds extensive applications in almost every field of science, and should be an invaluable adjunct to any industrial or scientific research laboratory.